



Grain Boundary Conductivity in Crystalline $\text{LiTi}_2(\text{PO}_4)_3$

by Jeff Wolfenstine

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14. ABSTRACT <p>This Technical Note suggests that the low values of Li-ion grain boundary conductivity in crystalline LiTi₂(PO₄)₃, compared to bulk Li-ion conductivity, are the result of a space charge region associated with grain boundaries and not a result of an amorphous phase along grain boundaries—as was previously suggested. This conclusion is based on microstructural evidence, a comparison of the activation energy for grain boundary conductivity, and recent results on doped polycrystalline oxygen-ion conductors containing no amorphous phases along grain boundaries.</p>					
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Recently, there has been a renewed interest in the development of high energy Li-Air batteries. One configuration involves the use of a Li anode in a non-aqueous electrolyte, which is separated from an aqueous electrolyte containing the air cathode by a solid state Li-ion conducting membrane. Several solid state polycrystalline Li-ion conductors, based on perovskite (1,2), garnet (3,4) and NASICON (Na super ion conductor) (5 through 12) structures, are under consideration as possible membrane materials. One of most widely investigated crystalline Li-ion conducting membrane materials, based on the NASICON structure, is $\text{LiTi}_2(\text{PO}_4)_3$ (5 through 10). In order to sinter crystalline $\text{LiTi}_2(\text{PO}_4)_3$ to the high relative densities required for use as a membrane and increase Li-ion conductivity, two approaches have been undertaken (5 through 10). The first is to use a doped material, $\text{LiM}_x\text{Ti}_{2-x}(\text{PO}_4)_3$ (where M=Al, Sc, Y and La) (5,6,9,10). The second is to use $\text{LiTi}_2(\text{PO}_4)_3$ containing a small amount of Li_2O or Li_3PO_4 or Li_3BO_3 (5,7,8). Previous investigations have suggested the total Li-ion conductivity, based on analysis of ac impedance data, of M-doped $\text{LiTi}_2(\text{PO}_4)_3$ (where M=Al, Sc, Y and La) and $\text{LiTi}_2(\text{PO}_4)_3$ containing a small amount of Li_2O or Li_3PO_4 or Li_3BO_3 was controlled by Li-ion grain boundary conductivity, which is about 1 to 2 orders of magnitude lower compared to Li-ion bulk conductivity (5 through 10). It has been suggested that for both polycrystalline M-doped $\text{LiTi}_2(\text{PO}_4)_3$ (where M=Al, Sc, Y and La) and $\text{LiTi}_2(\text{PO}_4)_3$ containing a small amount of Li_2O or Li_3PO_4 or Li_3BO_3 , that both approaches lead to the formation of a continuous amorphous film around the grains (5 through 10). It is the transport of Li-ions through this amorphous film which controls the sintering rate (i.e., densification) and grain boundary Li-ion conductivity, and hence, total Li-ion conductivity of the material (5 through 10).

This Technical Note suggests an alternative interpretation of what controls Li-ion grain boundary conductivity in polycrystalline M-doped $\text{LiTi}_2(\text{PO}_4)_3$ (where M=Al, Sc, Y and La) and $\text{LiTi}_2(\text{PO}_4)_3$ containing a small amount of Li_2O or Li_3PO_4 or Li_3BO_3 , based on the existing experimental data for these materials and a comparison to recent results for polycrystalline oxygen-ion conducting membranes. This result has implications not only for increasing the total Li-ion conductivity of NASICON based Li-ion conductors but, also for polycrystalline Li-ion conductors based on perovskite and garnet structures where the total Li-ion conductivity is also controlled by grain boundary Li-ion conductivity (1 through 5).

For the case of polycrystalline M-doped $\text{LiTi}_2(\text{PO}_4)_3$ (where M=Al, Sc, Y and La) and $\text{LiTi}_2(\text{PO}_4)_3$ containing a small amount of Li_2O or Li_3PO_4 or Li_3BO_3 , it is postulated that the reason for the low grain boundary Li-ion conductivity is not due to Li-ion transport through the grain boundary amorphous phase as previously suggested but, instead is through grain to grain contact where the resistance is determined by a space charge region associated with the grain boundary. The presence of the amorphous phase serves only to reduce the amount of grain/grain contacts, as shown in figure 1 (13). Evidence to support the above claim is as follows:

Firstly, no conclusive microstructural evidence for an amorphous phase along grain boundaries in polycrystalline M-doped $\text{LiTi}_2(\text{PO}_4)_3$ (where M=Al, Sc, Y and La) and $\text{LiTi}_2(\text{PO}_4)_3$ containing a small amount of Li_2O or Li_3PO_4 or Li_3BO_3 materials exists (5,7,9). For example, scanning

electron micrographs do not reveal any rounding of grain corners at multiple grain junctions (7,9), which is typical for material containing an amorphous boundary phase (14 through 16). Furthermore, no transmission electron micrographs showing evidence of an amorphous phase along the grain boundaries are presented.

Secondly, if a grain boundary phase controls grain boundary conductivity, then the activation energy for grain boundary conductivity should be different for chemically different boundary phases (13,17 through 19,20). This is in contrast to the experimental results where the activation for grain boundary conduction in the different M-doped $\text{LiTi}_2(\text{PO}_4)_3$ (where M=Al, Sc, Y and La) materials and $\text{LiTi}_2(\text{PO}_4)_3$ containing a small amount different additives such as; Li_2O or Li_3PO_4 or Li_3BO_3 all have nearly the same value (~ 0.36 eV [5]).

Thirdly, recent results for doped polycrystalline CeO_2 and ZrO_2 oxygen-ion conductors have shown that the oxygen-ion grain boundary conductivity is 2 to 3 orders of magnitude lower than for bulk oxygen-ion conductivity (13,19), in agreement with the results for M-doped $\text{LiTi}_2(\text{PO}_4)_3$ (where M=Al, Sc, Y and La) materials and $\text{LiTi}_2(\text{PO}_4)_3$ containing a small amount of Li_2O or Li_3PO_4 or Li_3BO_3 materials. For the case of these oxygen-ion conductors, detailed electron microscopy revealed clean grain boundaries (no amorphous phases along the boundaries). Any amorphous phase was located at triple junctions and not along grain boundaries. Thus, the presence of an amorphous phase along the grain boundaries is not required to account for low grain boundary ionic conductivity compared to bulk ionic conductivity. Maier et al., (13,17 through 19) have suggested that the major reason for the low grain boundary ionic conductivity in these materials is a result a space charge effect associated with grain boundaries compared to the bulk, where no space charge exists. The presence an amorphous phase serves only to reduce the fraction of grain/grain contacts (figure 1). The space charge model has successfully predicted the ratio of grain boundary conductivity/bulk conductivity, activation energy for grain boundary diffusion and the effect of aliovalent cation dopants on grain boundary conductivity in the doped polycrystalline CeO_2 and ZrO_2 oxygen-ion conductors (13,19).

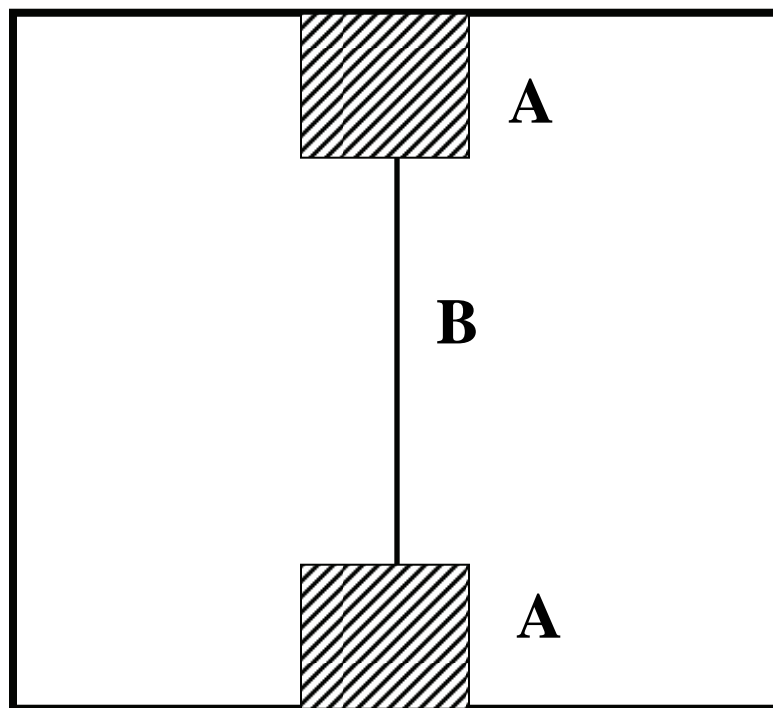


Figure 1. Schematic diagram of grain boundaries showing: a) amorphous phase and b) grain to grain contact (13).

In conclusion, from microstructural evidence similar values of the activation for grain boundary conductivity of the $\text{LiTi}_2(\text{PO}_4)_3$ material with different dopants and second phase materials, and from recent results on doped polycrystalline oxygen-ion conductors, where no amorphous phases along grain boundaries were observed, whose lower grain boundary oxygen-ion conductivity to bulk oxygen-ion conductivity can be explained by a space charge model, it is highly likely that the low value of Li-ion grain boundary conductivity compared to bulk Li-ion conductivity, reported previously in crystalline M-doped $\text{LiTi}_2(\text{PO}_4)_3$ (where M=Al, Sc, Y and La) and $\text{LiTi}_2(\text{PO}_4)_3$ containing a small amount of Li_2O or Li_3PO_4 or Li_3BO_3 materials, is through direct grain to grain contact where the resistance is controlled by a space charge region associated with the grain boundaries and not a result of an amorphous phase along grain boundaries, as previously suggested. The presence of any amorphous phase serves only to reduce the amount of grain/grain contacts. To conclusively confirm this suggestion, a very detailed investigation relating microstructure to conductivity in high density pure polycrystalline $\text{LiTi}_2(\text{PO}_4)_3$ and $\text{LiTi}_2(\text{PO}_4)_3$ containing a second phase is required. The results of this Technical Note have implications not only for increasing the total Li-ion conductivity of NASICON based Li-ion conductors but, also for polycrystalline Li-ion conductors based on perovskite and garnet structures, where their total Li-ion conductivity is also controlled by grain boundary Li-ion conductivity.

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